PATENT SPECIFICATION

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(19)

(54) PREPARATION OF ACETOXY ARYLENE SULPHONATES

(71)   We, UNILEVER LIMITED, a company organised under the laws of Great Britain, of Unilever House, Blackfriars, London E/C 4, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the preparation of certain reactive esters.

Esters of the general formula $CH_3CO.OR.SO_3M$, wherein R is an unsubstituted or substituted p-phenylene radical and M is an alkali metal, ammonium or substituted ammonium radical, are known to have the ability to enhance the bleaching action at low temperatures of per-salts. By the term "persalt" is meant those compounds more properly termed "peroxyhydrates" which contain hydrogen peroxide of crystallisation which is liberated when the substances are dissolved in water.

Examples of these substances are the alkali metal perborates, percarbonates, perpyrophosphates and persilicates.

Preferred esters of the group are sodium p-acetoxybenzene sulphonate and potassium p-acetoxybenzene sulphonate.

The manufacture of these reactive esters generally involves the following steps (for simplicity reasons the chemical reactions are shown below in relation to unsubstituted phenol):

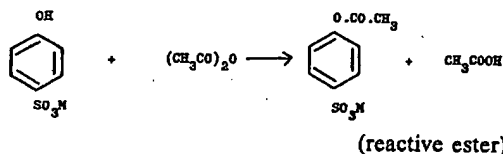a) Sulphonation of (substituted) phenol:
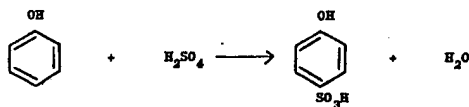
b) Neutralisation of the (substituted) phenol sulphonic acid:
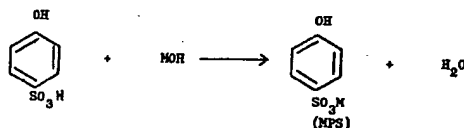
c) Drying of phenol sulphonate from b)
d) Acetylation of dry p-phenol sulphonate with acetic anhydride:

(reactive ester)

In a conventional process for preparing these reactive esters, the dry phenol sulphonate or substituted phenol sulphonate (MPS) is acetylated as a slurry with a liquid mixture of acetic anhydride and acetic acid.

The reactive ester is then isolated either by filtration and drying or by evaporation of the acetic acid and residual acetic anhydride. Whilst acetylation is quite straight forward, the recovery of the product from the resultant slurry poses problems. It is difficult to filter off the reactive ester which still has to undergo a drying operation. In an alternative method the acetic acid is evaporated from the slurry for which it has been found necessary to use a vacuum operated heavy-duty kneader/mixer. Even then the results are still rather poor as regards colour and odour.

It has now been found that the above difficulties can be overcome by applying a dry reaction between MPS and acetic anhydride in vapour form.

Accordingly the invention provides a process for preparing an ester of the general formula $CH_3CO.OR.SO_3M$ wherein R is an unsubstituted or substituted p-phenylene radical and M is an alkali metal, alkaline earth metal, ammonium or substituted ammonium radical, which comprises contacting a dry phenol sulphonate powder with acetic anhydride in vapour form.

The spray-dried phenol sulphonate is obtained from spray-drying the wet sulphonate slurry from reaction (b) using a spray tower.

In contrast to the difficulties experienced in the removal of by-product acetic acid from the product in the slurry process, acetic acid and any excess acetic-anhydride in the dry process of the invention can be easily removed from the reactive ester product by flushing the reactor with an inert gas, such as nitrogen.

As the acetylation reaction is exothermic, the generated heat has to be dissipated in the vapour/gas stream and/or through the reaction wall. Efficient absorption of acetic anhydride vapour and maintenance of a good temperature control, depending on good mixing of the solids with the vapour stream, are important factors for a high conversion. It is therefore important in carrying out the process of the invention to keep the whole charge of solids moving, preferably fluidised with substantially no "dead" pockets of powder. This latter can be achieved by proper selection of the gas distributor. Hence in one preferred embodiment of the invention the dry phenol sulphonate (MPS) powder is fluidised with a gas comprising acetic anhydride vapour in a fluidised bed reactor. Any excess of acetic anhydride and the by-product acetic acid is removed from the reaction product with a stream of an inert gas, e.g. nitrogen. Dissipation of heat in the vapour/gas stream can be improved by diluting the acetic anhydride with a diluent gas, such as nitrogen or acetic acid vapour. It has been found that within a wide range of concentration, the presence of acetic acid vapour or nitrogen does not affect the efficiency of acetic anhydride absorption or the final conversion of phenol sulphonate to the reactive ester. Acetic anhydride/acetic acid vapour mixtures containing up to 60% v/v acetic acid can be used without significant loss of reactivity.

Though various techniques can be applied to dry the phenol sulphonate, such as drum drying or spray drying, the present process prefers the use of spray-dried phenol sulphonate, in view of its large surface area for contact with the acetic anhydride vapour and in view of its spherical particles, which readily fluidise.

The process of the invention can be used to manufacture the "plain" reactive ester, which generally needs to be granulated, before use in a detergent powder, to improve its storage stability (see Br. Pat. Spec. 864,798). The term "plain" is used here to indicate the substantially pure and non-stabilised reactive ester.

The process of the invention can also be used to manufacture directly a reactive ester combined with a stabilising agent as disclosed in Br. Pat. Spec. 963,135, such as disodium dihydrogen pyrophosphate.

Since acetylation of dried MPS in a fluidised bed according to the invention causes little, if any, attrition, the stabilising agent for the reactive ester can be mixed with the dry MPS before acetylation, without the risk of being changed during the acetylation process, so that a stabilised product is obtained without the need for an additional granulating process.

While it is possible to use any intimate mixture of the stabilising agent and MPS, it is preferred to use an intimate mixture of MPS and the stabilising agent, which is prepared by spray-drying an aqueous slurry comprising a mixture of phenol sulphonate and the stabilising agent e.g. sodium phenol sulphonate and disodium dihydrogen pyrophosphate.

A convenient method for preparing such slurry is by mixing phenol sulphonic

acid and tetra sodium pyrophosphate in such proportions to neutralise the sulphonic acid with formation of disodium dihydrogen pyrophosphate.

Accordingly in another preferred embodiment of the invention the process comprises the spray-drying of a p-phenol sulphonate including a stabilising agent and acetylating the spray-dried phenol sulphonate with acetic anhydride vapour in a fluidised bed to produce a stabilised reactive ester of the general formula as hereinbefore defined.

A contemplation will now be given on the factors influencing the performance of a fluidised bed reactor for use in the process of the invention.

Fluidisation requires that the bed of powder be suspended in the gas stream, i.e. that the pressure drop through the bed be equal to the weight of powder per unit area. The minimum fluidisation velocity to give this pressure drop is dependent on the physical properties of the powder and on the composition and temperature of the fluidising gas.

It is preferable to work at about twice the minimum fluidisation velocity. The excess of gas forms bubbles which create turbulence in the bed, giving good mixing of the powder and improving the temperature control, and reduces the risk of defluidisation due to porosity variations across the gas distributor. Bubbling, however, also causes a proportion of the gas to by-pass the powder without reacting.

Powders with a wide particle-size distribution are fairly readily produced by spray-drying and allow fluidisation at low gas velocities. However, it is desirable to minimise "fines" in the interest of product storage-stability, though a sufficiently stable product is obtained if a spray-dried p-phenol sulphonate/stabilising agent powder is acetylated in a fluidised bed.

Particle shape is also very important; particles should preferably be spherical rather than irregular and separate rather than aggregate. Aggregates are very difficult to fluidise unless mechanical agitation is used, and this tends to break the larger particles and produce fines. With spray-dried phenol sulphonate powder and with no mechanical agitation in the reactor, less than 5% of the charge is generally broken to fines by attrition and these are normally elutriated from the reactor in the gas stream. With mechanical agitation, up to 40% of even the best powders may be broken to fines.

The efficiency of acetic anhydride absorption increases with increasing reactor temperature and, in terms of temperature control, the acetylation reaction may be divided roughly into two stages.

In the first stage, during which one mole of acetic anhydride per mole of phenol sulphonate (MPS) is passed into the reactor and about 65% MPS is acetylated, the reaction is very fast and the acetic anhydride input-rate controls the rate of reaction. The temperature of the bed will be approx. 150—185°C during this stage but once the reaction has started the main problem is to prevent the liberated heat of reaction from overheating the bed.

In the second stage, during which a further 2 moles of acetic anhydride per mole of MPS are passed into the reactor, the conversion rises to about 85% and the reaction is much slower than in the first stage, and is controlled by either:
 (i) the chemical reaction-rate, when the concentration of MPS in the powder is low, or
(ii) the rate of diffusion of acetic anhydride into the particles.
During this stage the temperature tends to fall and it is desirable to supply extra heat to keep the reaction at about 170—210°C. Local overheating due to poor mixing could easily lead to serious discolouration of the product. Hence, good temperature control and therefore good mixing in the bed is important. Hence the overall bed temperature during acetylation will lie between 150—220°C. Preferably a temperature range of about 170°C to about 205°C should be maintained in order to achieve a quick conversion without the danger of local overheating.

Heat can be dissipated for the reactor either through the walls or by restricting the preheating of the gas stream. However, the experience is that the major part of the heat of reaction should be conveniently dissipated in the gas stream.

Hence, although MPS can be fluidised with undiluted acetic anhydride vapour, the reaction would be so fast that temperature control could be difficult. Consequently, it is preferable to dilute the acetic anhydride with a diluent gas, e.g. acetic acid and/or nitrogen, preferably acetic-acid.

The possible advantages of using acetic-acid as diluent are:

(i) the excess of acetic anhydride contaminated with acetic-acid can be recycled for use without complete fractionation;

(ii) the greater heat capacity of acetic-acid as compared with that of nitrogen, makes it the more effective means of removing heat from the reactor and higher concentrations of acetic anhydride can be used, thereby shortening the reaction time.

Another variable worth considering is bed depth. One would expect that increasing the bed depth would also increase the efficiency of acetic anhydride absorption in a fluidised bed, since the gas stream would have a longer time in contact with the powder. However, the physical stability of a fluidised bed depends on there not being too great a pressure drop through the reactor. Too large a pressure drop results in the growth of large bubbles which pass through the bed without adequate contact with the powder.

Experiments have shown that in a 30 cm diameter reactor at bed depths of 33, 51 and 66 cm, corresponding to charges of 9.1 13.6, 18.2 kg respectively, there was improved absorption from 33 to 51 cm but no further improvement from 51 to 66 cm. In another experiment using a 25 cm diameter reactor the effect of varying the bed depth up to 87 cm was also investigated. Generally it can be said that a bed depth/diameter ratio of about 1.5 would give an efficient absorption of acetic anhydride vapour.

A further description of the process of the invention will now be given with the help of the attached figure 1. In this figure the fluidised bed reactor (1) is fitted with a gas distributor (2) at the base and is jacketed (3). High pressure steam (4) or cooling water (5) could be circulated through this jacket as required to assist in heating or cooling the bed of powder. Thermocouples (T) are fitted in the reactor to check for temperature gradients. A pipe (6) is fitted near the base of the reactor for withdrawing samples from the centre of the bed for analysis to record the course of the reaction.

Prior to the acetylation, the dried MPS powder is preheated by passing through the bed via line (7) air which has been heated in a furnace (8). At this stage heat can also be supplied from the high pressure steam jacket. When the MPS powder has reached the reaction temperature, the air is flushed out of the reactor with an inert gas, e.g. nitrogen from line (9) to prevent possible formation of explosive gas mixtures. The reactor is then ready for the acetylation.

Acetic anhydride is pumped through a preheater (10) fed with steam through steam line (20) to evaporators (11 and 12) operated in series. Preheated nitrogen (used here as diluent) is fed into the acetic anhydride vapour at the catchpot (13) after the second evaporator, and the gaseous mixture is passed to the reactor via superheater (14).

Exhaust gas from the reactor (1) is passed through a cyclone separator (15) to two condensers (16 and 17) in series. Dust carried out of the reactor is recovered from the cyclone separator. Liquid acetic acid/acetic anhydride is passed through a cooler (21) and the final traces of acetic anhydride and the by-product acetic acid, are scrubbed from the nitrogen before it is released to the atmosphere. A sodium carbonate solution can be used in the scrubber (18).

After the appropriate quantity of acetic anhydride has been passed through the reactor, the metering pump (19) is shut off and the nitrogen flow continues to purge the acetic anhydride from the reactor to free the reactive ester obtained from any remaining acetic anhydride and acetic acid. The reactive ester product can be cooled by passing cold air through the reactor and cold water through the reactor jacket. Final conversions of up to about 90% can be achieved as is shown in the following Examples.

Examples I—V.

A series of five experiments was carried out in a 70 cm diameter reactor with a sand-bed gas distributor. In each case the fluidising gas was a mixture of acetic anhydride vapour with nitrogen diluent.

The reaction conditions are given in Table I.

TABLE 1

Acetylation of a spray-dried sodium p-phenol sulphonate
(SPS) disodium dihydrogen pyrophosphate mixture

Example No.	I	II	III	IV	V
Reactor charge ⎰ kg	150	145.6	169	156	141
⎱ Mole SPS	420	416	474	450	388
Inlet gas composition, mole %					
Acetic anhydride	34.8	35.0	26.8	25.6	27.0
Nitrogen	65.2	65.0	73.2	74.4	73.0
Superficial gas velocity, cm/sec.	8.5	9.1	11.5	12.2	12.3
Initial powder temp., °C	176	183	170	181	186
Max. temp. at base of reactor, °C	198	258	236	197	212
Max. temp. at top of charge, °C.	198	200	214	197	212
Average bed temp. in reactor during experiment, °C	189	196	198	189	196

In the second and third experiments, the temperature near the base of the reactor reached a very high level during an early part of the reaction. This suggests that while there was very good absorption of the acetic anhydride vapour as soon as it met the fluidised SPS powder, the mixing of the charge of powder was not good enough to distribute the heat of reaction evenly through the reactor. The product from the second experiment, in which the temperature reached 258°C for a short time, was discoloured.

At a higher gas velocity of about 12.2—12.3 cm/sec., the temperature control was much better and no temperature gradients were observed in the reactor.

The conversion of the SPS to the reactive ester, sodium p-acetoxy benzene sulphonate, was measured in samples withdrawn from the reactor during the experiments and is shown graphically as a function of mole ratio acetic anhydride input to SPS charge in figure 2, and as a function of reaction time in figure 3. Although the curves show some variation over the five experiments, they are related to the gas velocity through the reactor.

The first two experiments, at low gas velocity, did not agree with each other or with the later three experiments. Both experiments gave about 80% conversion although the conversion curves diverged.

The final three experiments, at higher gas velocity, were in good agreement with each other and gave a final conversion in the region of 85—90%, depending on the mole ratio of acetic anhydride passed through the reactor to the charge of SPS (2.2—3.4).

Examples VI—IX.

A series of four experiments was carried out in a 30 cm diameter reactor fitted with a porous plate at the base and charged with 9 kg of spray-dried sodium p-phenol sulphonate.

The fluidising gas was a mixture of acetic anhydride, acetic acid and nitrogen, the total acetic anhydride usage amounting to approximately 1.3 moles per mole of reactive ester formed.

In carrying out the process the temperature of the bed was in each case raised initially to 130—140°C to ensure that the acetic anhydride vapour would not condense in it, causing caking to arise, and to promote the acetylation. A mixture of acetic anhydride and acetic acid was metered to a steam jacketed evaporator.

and the vapour generated in the evaporator was mixed with nitrogen and passed through a steam-jacketed stainless steel pipe to superheat it. The superheated vapour was then passed through the reactor bed and the excess acetic anhydride and acetic acid vapour condensed out of the effluent gas. After a predetermined reaction period the acetic anhydride/acetic acid flow was shut off, and the bed purged with nitrogen to remove excess acetylating agent. The product was then discharged as a free flowing powder.

A series of acetylations was carried out in which the vapour inlet temperature was varied from 160°C to 180°C, and the acetic anhydride concentration in the feedstock varied from 28% to 48% (w/w).

It was noted that when the vapour was passed into the bed at 180°C, the bed temperature rose initially to 173—183°C depending on the concentration of anhydride in the vapour. With vapour at 160°C, the bed temperature rose to 163—175°C.

The results given in the following Table II indicate that the temperature of the inlet vapour had little effect on the conversion when the higher concentration of anhydride was used. With the lower acetic-anhydride concentration, the vapour temperature had a more pronounced effect on conversion, and a considerable improvement in reaction rate was observed when the vapour was raised from 160°C to 180°C.

TABLE II

Acetylation of spray-dried sodium phenol sulphonate

Example No.	Acetic-anhydride % (w/w)	Inlet vapour Temp. °C	Conversion % after			
			1h	1½h	2h	2½h
VI	47.1	178	84.7	89.1	91.0	90.4
VII	48.6	160	82.8	87.5	90.2	92.5
VIII	30.6	182	69.5	81.2	86.8	88.9
IX	28.2	160	69.0	75.5	77.9	82.0

WHAT WE CLAIM IS:—

1. A process for preparing an ester of the general formula $CH_3CO.OR.SO_3M$, wherein R is an unsubstituted or substituted p-phenylene radical and M is an alkali metal, alkaline earth metal, ammonium or substituted ammonium radical, which comprises contacting a dry p-phenol sulphonate powder with acetic anhydride in vapour form.

2. A process according to claim 1, wherein the dry phenol sulphonate powder is fluidised with a gas comprising acetic anhydride vapour in a fluidised bed reactor at a temperature of 150—220°C.

3. A process according to claim 2, wherein the fluidising gas comprises a mixture of acetic anhydride vapour and a diluent gas, selected from nitrogen and acetic acid vapour, and mixtures thereof.

4. A process according to claim 2, wherein the bed temperature is from about 170°C to 205°C.

5. A process according to claim 2, wherein the dry phenol sulphonate is spray-dried phenol sulphonate.

6. A process according to claim 1 or 2, wherein the dry phenol sulphonate is mixed with a stabilising agent.

7. A process according to claim 6, wherein the stabilising agent is disodium dihydrogen pyrophosphate.

8. A process according to claim 6 or 7, wherein the dry phenol sulphonate/stabilising agent mixture is obtained from spray-drying an aqueous slurry comprising phenol sulphonate and the stabilising agent.

9. A process according to claim 1 substantially as herein described.

10. A process of preparing an ester of general formula $CH_3CO.OR.SO_3M$ substantially as described in any of the Examples.

11. An ester of general formula $CH_3CO.OR.SO_3M$ prepared by the process of any preceding claim.

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